

SUPPORTING INFORMATION

Stable isotope analysis of intact oxyanions using electrospray

Quadrupole-Orbitrap mass spectrometry

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Supplemental methods

Bulk isotopic composition. The isotopic compositions of in-house reference standards of sulfate salts were obtained by conventional IRMS methods. Sulfur-34 isotope measurements were done on an elemental analyzer-isotope ratio mass spectrometer (EA-IRMS) using the same Na_2SO_4 stock solutions used for ESMS measurements. The solution was pipetted directly into tin capsules and dried overnight at 70°C. Results were normalized to international reference materials IAEA-S-1, IAEA-S-2, and IAEA-S-3 with $\delta^{34}\text{S}$ values taken from Brand et al.¹ as well as in-house Na_2SO_4 and seawater solutions. The precisions for $\delta^{34}\text{S}_{\text{SO}_4}$ measurements are better than 0.2 ‰.

Oxygen-18 isotope measurements were analyzed on a thermal-conversion (TC) EA-IRMS. Sulfate in solution was converted to barite through precipitation with BaCl_2 . The barite was cleaned using 6M HCl, to dissolve any barium carbonate co-precipitate, and then rinsed three times with deionized water and dried in the oven overnight. Barite was weighed into silver capsules and pyrolyzed in a TC/EA, and measured via continuous helium flow on a Delta V mass spectrometer. Samples were run for $\delta^{18}\text{O}_{\text{SO}_4}$ ten times and the average and standard deviation presented. These samples were bracketed with NBS-127 ($\delta^{18}\text{O}_{\text{SO}_4} = 8.6 \text{ ‰}_{\text{VSMOW}}$), which was used to correct for drift over the course of the run. The isotopic composition of sulfate and nitrate materials determined by conventional isotope-ratio analysis are summarized in Table S2.

Supplemental tables

Table S1. Existing methods for isotopic analysis of sulfate and nitrate

Method*	Conversion and Analyte	Isotope Ratio	Precision (‰; 2sd)	Sensitivity	Throughput (samples/day)	Reference
MC-ICP-MS	Na ₂ SO ₄	$\delta^{34}\text{S}$, $\Delta^{33}\text{S}$	$\delta^{34}\text{S}$: 0.08-0.15; $\Delta^{33}\text{S}$: 0.1-0.3	> 5 nmol sulfur, typically 20 nmol	< 20	Paris et al. (2013) ²
dual-inlet IRMS	Ag ₂ S → SF ₆	$\delta^{34}\text{S}$, $\Delta^{33}\text{S}$, $\Delta^{36}\text{S}$	$\delta^{34}\text{S}$: ~0.2, $\Delta^{33}\text{S}$: ~0.02	10 μmol	< 10	Hulston and Thode (1965) ³
EA-IRMS	Sulfate → SO ₂	$\delta^{34}\text{S}$	> 0.05	> 0.1 μmol sulfur	< 60	Thode et al. (1961) ⁴
IRMS	Sulfate → O ₂	$\delta^{18}\text{O}$, $\Delta^{17}\text{O}$	$\delta^{18}\text{O}$: 1.6, $\Delta^{17}\text{O}$: 0.1 (2 for smaller samples)	> 17 μmol sulfur	> 12	Bao and Thiemens (2000) ⁵
TC/EA-IRMS	Sulfate → CO ₂ or CO	$\delta^{18}\text{O}$	$\delta^{18}\text{O}$: 0.1-0.3	0.5 μmol	< 40	Boschetti & Iacumin (2005) ⁶
GB-IRMS	Nitrate → N ₂ O (bacterial/chemical conversion)	$\delta^{15}\text{N}$, $\delta^{18}\text{O}$, $\Delta^{17}\text{O}$	$\delta^{15}\text{N}$: 0.2; $\delta^{18}\text{O}$: 0.3; $\Delta^{17}\text{O}$: 0.2-0.5	> 2 nmol nitrate, typically 5-20 nmol	< 120	Sigman et al. (2001) ⁷ , Kaiser et al. (2007) ⁸ , Weigand et al. (2016) ⁹
TC/EA-IRMS	Nitrate → N ₂ , O ₂	$\delta^{15}\text{N}$, $\delta^{18}\text{O}$, $\Delta^{17}\text{O}$	$\delta^{15}\text{N}$: 0.2; $\delta^{18}\text{O}$: 0.3, $\Delta^{17}\text{O}$: 1.0	> 1 μmol nitrate	< 60	Michalski et al. (2002) ¹⁰ , Böttcher et al (1990) ¹¹
ESMS	Na ₂ SO ₄	$\delta^{34}\text{S}$, $\delta^{33}\text{S}$, $\delta^{36}\text{S}$, $\delta^{18}\text{O}$, $\Delta^{34}\text{S}^{18}\text{O}$	$\delta^{34}\text{S}$: <2, $\delta^{18}\text{O}$: <2	< 1 nmol sulfate (data acquisition)	~10 (manual sample changing)	This study
ESMS	KNO ₃	$\delta^{15}\text{N}$, $\delta^{18}\text{O}$, $\delta^{17}\text{O}$	$\delta^{15}\text{N}$: <2, $\delta^{18}\text{O}$: <2	< 1 nmol nitrate (data acquisition)	~ 10 (manual sample changing)	This study

*EA: elemental analyzer, ICP: inductively coupled plasma, IRMS: isotope-ratio mass spectrometry, MC: multi-collector, TC: thermal-conversion, GB: gas bench

Table S2. Description of the sulfate and nitrate materials used in this study, including their isotopic composition as determined by IRMS.

Name	Provider	Origin	$\delta^{18}\text{O}$ (‰ _{VSMOW} ; SD)	$\delta^{34}\text{S}$ (‰ _{VCDT} ; SD)	Purity and comments
Antarctica	G. Rossman, Caltech	McMurdo Station, Antarctica	+8.73±0.82(n=10)	+21.44 ±0.15 (n=5)	likely anhydrous; obtained as a powder
Cedar Lake	Saltext, Tx (Cooper Natural)	Cedar Lake, Texas, USA	+12.45±0.44 (n=10)	+10.92±0.2 (n=2)	99.8%; 0.01% water
Chaplin	Airborne Industrial Minerals	Chaplin, Saskatchewan, Canada	+11.54±1.14 (n=9)	+3.15±0.2 (n=2)	99.57%; 0.15% MgSO ₄ ; 0.013% water
Laguna del Rey	Peñoles	Laguna del Rey, Coahuila, Mexico	+12.92±0.69 (n=9)	+13.91±0.2 (n=2)	99.90%
Mexico	Macron, 8024-04, Batch 0000177887	Made in Mexico	+8.24±0.88 (n=10)	-0.97±0.2 (n=2)	99.20%
Rio Tiron	Crimidesa, Lot #19-0579	Minera Rio Tiron, Burgos, Spain	+13.97±0.69 (n=10)	+12.61±0.2 (n=2)	99.8%; 0.01% water;
Soda Lake	G Rossman, Caltech	Soda Lake, Carrizo Plain, San Luis Obispo Co., California, USA	+11.14±0.57 (n=9)	-9.76±0.09 (n=5)	Thénardite; likely anhydrous; rocks were ground into a powder
Synthetic India	Sigma Aldrich, 239313-500G Lot # SLBR3461V	synthetic inorganic (manufactured in India)	+11.86±0.33 (n=10)	+1.04±0.2 (n=2)	99.90%
Trona	Searles Valley Minerals	Trona, California, USA	+19.76±0.64 (n=10)	+14.69±0.2 (n=2)	99.5%; 0.10% Na ₂ CO ₃ , 0.34% NaCl
			$\delta^{18}\text{O}$ (‰ _{VSMOW} ; SD), $\delta^{17}\text{O}$ (‰ _{VSMOW} ; SD)	$\delta^{15}\text{N}$ (‰ _{air N2} ; 2SD)	
USGS32	Reston Stable Isotope Laboratory – USGS (Reston, Virginia, USA)	USGS32 is a dried potassium nitrate salt, prepared by J. K. Böhlke in 1992 via dissolving and recrystallizing a mixture of normal reagent salt and ¹⁵ N-enriched salt.	+25.55±0.2; 13.01±0.35	+180 exactly	Böhlke et al. performed ¹⁸ O analysis using a TC/EA by on-line reduction with carbon. IRMS of ¹⁵ N/ ¹⁴ N was performed after combustion/reduction to N ₂ . ^{12,13} $\delta^{17}\text{O}$ provided by Andrew Schauer, Univ. Washington. USGS34 and USGS35 were used to calibrate $\delta^{17}\text{O}$ using the bacterial denitrifier method and thermal decomposition.
USGS34	Reston Stable Isotope Laboratory – USGS (Reston, Virginia, USA)	Prepared by equilibrating nitric acid with $\delta^{18}\text{O}$ depleted Antarctic snow-melt water and subsequent neutralization with KOH	-27.84±0.3, -14.55	-1.8±0.1	Prepared and characterized similar to USGS32 by Böhlke et al. ¹⁰ ¹⁷ O was measured by off-line decomposition to O ₂ .

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